

### 3 Relativistic wave equations

#### 3.1 Klein-Gordon

The Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \quad (3.1)$$

$$H = \frac{p^2}{2m} + V \quad (3.2)$$

contains first derivatives with respect to time,  $t$ , and second derivatives with respect to  $(xyz)$ . We now wish to handle all four coordinates  $(x_1 x_2 x_3 x_4)$  on equal footing.

The **Klein-Gordon** equation was introduced by **Fock** (1926ab), **Gordon** (1926), **Klein** (1926-1927), **Kudar** (1926) and Schrödinger (1926). We wish to satisfy

$$E^2 = c^2 p^2 + m^2 c^4 \quad (3.3)$$

(Compare with (1.40),  $m = m_0$ ).

Taking the square root, we would get

$$H = \sqrt{c^2 p^2 + m^2 c^4} + V \quad (3.4)$$

but the problem would be to actually take the square root.

Reorganizing, we get

$$(E - V)\psi = \sqrt{c^2 p^2 + m^2 c^4}\psi \quad (3.5)$$

Squaring (operating twice)

$$\underline{\underline{(E - V)^2\psi}} = (E^2 - 2EV + V^2)\psi = \underline{\underline{(c^2 p^2 + m^2 c^4)\psi}} \mid : 2mc^2 \quad (3.6)$$

$$\left[ \frac{p^2}{2m} + \frac{1}{2}mc^2 - \frac{1}{2mc^2}(E^2 - 2EV + V^2) \right] \psi = 0 \mid E = mc^2 + \epsilon$$

$$\left[ \frac{p^2}{2m} + \frac{1}{2}mc^2 - \frac{1}{2mc^2}(m^2 c^4 + \underline{\underline{\underline{\underline{2\epsilon mc^2}}}} + \epsilon^2 - \underline{\underline{\underline{2mc^2 V}}} - 2\epsilon V + V^2) \right] \psi = 0$$

$$\left[ \frac{p^2}{2m} + \underline{\underline{\underline{V - \epsilon}}} - \underbrace{\frac{1}{2mc^2}(\epsilon - V)^2}_{h_m \text{ (mass-velocity) of Pauli}} \right] \Psi = 0 \quad (3.7)$$

$h_m$  is often expressed as

$$h_m = -\frac{p^4}{8m^3 c^2}$$

The external electromagnetic field  $\underline{A}, V$  can be included through the *minimal substitution*  $\underline{p} \rightarrow \underline{p} - \frac{q}{c}\underline{A}$ ,  $q$  being the charge of the particle. For  $e \equiv |e|$ , (3.6) becomes, for electrons,

$$\underline{\underline{(E - V)^2\psi}} = \left[ c^2 \left( \underline{p} + \frac{e}{c} \underline{A} \right)^2 + m^2 c^4 \right] \psi \quad (3.8)$$

[This is valid in the Gauss-cgs system of units or in atomic units. In SI, use  $\underline{p} \rightarrow \underline{p} - q\underline{A}$ ]

For a free particle, replacing

$$E \rightarrow i\hbar \frac{\partial}{\partial t} \quad (3.9)$$

and introducing the **d'Alembert** operator

$$\square = \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}, \quad (3.10)$$

$$\begin{aligned} & \left[ -\hbar^2 \frac{\partial^2}{\partial t^2} - m^2 c^4 + \hbar^2 c^2 \nabla^2 \right] \psi = 0 \quad | : \hbar^2 c^2 \\ & \left[ \square - \frac{m^2 c^2}{\hbar^2} \right] \psi = 0 \end{aligned} \quad (3.11)$$

The equation (3.7) is good for a *pionic* atom, see e.g. **K-C Wang et al.** PRA22(1980), 1072. It gives a wrong answer for the fine structure of *electronic* atoms<sup>3</sup>.

Multiply now (3.11) from left by  $\psi^*$ :

$$\begin{aligned} \psi^* \left[ \square - \frac{m^2 c^2}{\hbar^2} \right] \psi &= 0, \quad \text{and} \quad | + \\ \left[ \square - \frac{m^2 c^2}{\hbar^2} \right] \psi^* \psi &= 0 \quad | - \\ \psi^* (\square \psi) - (\square \psi^*) \psi &= 0 \end{aligned} \quad (3.12)$$

Using the definition of  $\square$

$$\psi^* (\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}) \psi - \left[ (\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}) \psi^* \right] \psi = 0 \quad (3.13)$$

As

$$\psi^* (\psi'') - (\psi^*)'' \psi = [\psi^* \psi' - (\psi^*)' \psi]' \quad (3.14)$$

and

$$\psi^* (\nabla^2 \psi) - \psi (\nabla^2 \psi^*) = \nabla \cdot [\psi^* \nabla \psi - \psi (\nabla \psi^*)] \quad (3.15)$$

we get the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \underline{j} = 0 \quad (3.16)$$

where

$$\rho(\underline{r}, t) = \frac{i\hbar}{2mc^2} \left( \psi^* \frac{\partial \psi}{\partial t} - \frac{\partial (\psi^*)}{\partial t} \psi \right) \quad (3.17)$$

$$\underline{j}(\underline{r}, t) = -\frac{i\hbar}{2m} (\psi^* \nabla \psi - (\nabla \psi^*) \psi) \quad (3.18)$$

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<sup>3</sup>The proof is left as an exercise for the reader

reduce to the right non-relativistic limit (see e.g. Kvantkemi I, p. 20-21). Now the  $\rho$  is still real, but not necessarily positive definite. Replace in (3.17)  $i\hbar\frac{\partial}{\partial t} \rightarrow E \Rightarrow$

$$\rho = \frac{E}{mc^2}|\psi|^2. \text{ Now, if } E < 0, \rho < 0 \quad (3.19)$$

### 3.2 Dirac

We are searching for an equation of the form

$$i\hbar\frac{\partial}{\partial t}\psi = H\psi \quad (3.20)$$

Because of the first derivative  $\frac{\partial}{\partial t}$ , we would like to have first derivatives  $\frac{\partial}{\partial x}$  etc. as well. Note that the series expansion of the square root in

$$(E - V)\psi = mc^2\sqrt{1 + p^2/c^2}$$

would contain *all* powers of  $(p^2/c^2)$ .

Suppose now that the Hamiltonian is linear in all  $\frac{\partial}{\partial x_\mu}$  and that the wave function  $\Psi$  has  $N$  components,

$$\Psi = \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_N \end{pmatrix} \quad (3.21)$$

Then the most general free-particle wave equation is

$$i\hbar\frac{\partial}{\partial t}\Psi_n = \sum_{l=1}^N [c\underline{\alpha}_{nl} \cdot \underline{p} + \beta_{nl}mc^2]\Psi_l \quad (3.22)$$

where  $n$  runs from  $1 \dots N$ , and

$$\underline{\alpha}_{nl} \cdot \underline{p} = -i\hbar[(\alpha_{nl})_x \frac{\partial}{\partial x} + (\alpha_{nl})_y \frac{\partial}{\partial y} + (\alpha_{nl})_z \frac{\partial}{\partial z}] \quad (3.23)$$

In terms of the  $N \times N$  matrices  $\underline{\alpha}$  and  $\underline{\beta}$ ,

$$i\hbar\frac{\partial}{\partial t}\Psi = [-i\hbar c\underline{\alpha} \cdot \nabla + \beta mc^2]\Psi \equiv h_D\Psi \quad (3.24)$$

with the Dirac Hamiltonian

$$h_D = c\underline{\alpha} \cdot \underline{p} + \beta mc^2 \quad (3.25)$$

The  $D$  in  $h_D$  stands for Dirac.

The components of  $\alpha$  are the  $N \times N$  matrices ( $N \geq 4$ , see below)  $\alpha_x, \alpha_y$  and  $\alpha_z$ . In order for  $h_D$  to be Hermitian,  $\underline{\alpha}$  and  $\beta$  must be Hermitian:

$$\underline{\alpha}^\dagger = \underline{\alpha}, \quad \beta^\dagger = \beta \quad (3.26)$$

For all points in space-time to be equivalent,  $\underline{\alpha}$  and  $\beta$  must be constant and dimensionless. Consequently they commute with  $\underline{r}$  and  $\underline{p}$ .

We still want to satisfy

$$E^2 = c^2 p^2 + m^2 c^4$$

for all components  $\psi_1 \dots \psi_N$ :

$$-\hbar^2 \frac{\partial^2}{\partial t^2} \Psi = [-\hbar^2 c^2 \nabla^2 + m^2 c^4] \Psi \quad (3.27)$$

Then the Dirac equation

$$h_D \Psi = i\hbar \frac{\partial}{\partial t} \Psi$$

will connect the different components while every individual component,  $\psi_i$ , will satisfy the Klein-Gordon (K-G) equation (3.27).

### 3.2.1 Why must $N \geq 4$ ?

Starting from

$$\begin{aligned} \beta \alpha_i &= -\alpha_i \beta \quad |\beta \times \\ \alpha_i &= \underbrace{-\beta}_A \underbrace{\alpha_i \beta}_B \quad (\text{as } \beta^2 = \mathbf{I}) \end{aligned}$$

we see that

$$\begin{aligned} \text{Tr } AB &= \text{Tr } BA \\ \text{Tr } \alpha_i &= -\text{Tr } (\alpha_i \beta) \beta \quad |\beta^2 = \mathbf{I} \\ &= -\text{Tr } \alpha_i \\ &= 0 \end{aligned}$$

The  $\alpha_i$  were  $\pm 1$ . We have the same number of both  $\Rightarrow N$  must be even. On page 17 it was shown that 2 was too small  $\Rightarrow N \geq 4$ .  $\square$

### 3.2.2 Properties of Dirac matrices

Multiply now

$$(i\hbar \frac{\partial}{\partial t} - h_D) \Psi = 0$$

from the left by the operator  $i\hbar \frac{\partial}{\partial t} + h_D \Rightarrow$

$$(-\hbar^2 \frac{\partial^2}{\partial t^2} - h_D^2) \Psi = 0$$

in other words

$$-\hbar^2 \frac{\partial^2}{\partial t^2} \Psi = \left[ -\hbar^2 c^2 \sum_{i,j=1}^3 \frac{1}{2} (\alpha_i \alpha_j + \alpha_j \alpha_i) \frac{\partial^2}{\partial x_i \partial x_j} - i \hbar c \sum_{i=1}^3 (\beta \alpha_i + \alpha_i \beta) \frac{\partial}{\partial x_i} + m^2 c^4 \beta^2 \right] \Psi \quad (3.28)$$

where we have used the fact that  $[\frac{\partial}{\partial x_i}, \frac{\partial}{\partial x_j}] = 0$ .

From (3.27),

$$-\hbar^2 \frac{\partial^2}{\partial t^2} \Psi = [-\hbar^2 c^2 \nabla^2 + m^2 c^4] \Psi$$

$$\begin{cases} \alpha_i \alpha_j + \alpha_j \alpha_i = 2 \delta_{ij} \mathbf{I} \\ \beta \alpha_i + \alpha_i \beta = 0 \\ \beta^2 = \mathbf{I} \end{cases} \quad (3.29)$$

$\mathbf{I}$  being the  $N \times N$  unit matrix. Because  $\underline{\alpha}$  and  $\beta$  were Hermitian, their eigenvalues are real. According to (3.29), the squares of these eigenvalues equal 1. Hence the eigenvalues are  $\pm 1$ . Dirac noticed that (3.29) is satisfied by

$$\beta = \begin{pmatrix} \mathbf{I} & \\ & -\mathbf{I} \end{pmatrix} \quad (3.30)$$

$$\underline{\alpha} = \begin{pmatrix} 0 & \sigma \\ \underline{\sigma} & 0 \end{pmatrix} \quad (3.31)$$

where

$$\mathbf{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (3.32)$$

### 3.3 Some properties of the Dirac equation

#### 3.3.1 Solutions with $\pm E$

For a free particle,

$$[h_D, \underline{p}] = 0 \quad (3.33)$$

and hence the two operators have simultaneous eigenfunctions  $\Psi(\underline{p}, x)$ :

$$\begin{aligned} \hat{\underline{p}} \Psi &= \underline{p} \Psi \\ h_D \Psi &= E(\underline{p}) \Psi \end{aligned} \quad (3.34)$$

Operating again with  $h_D$ ,

$$h_D^2 \Psi = E(\underline{p})^2 \Psi \quad (3.35)$$

with the solutions

$$h_D \Psi_{\pm} = \pm E(\underline{p}) \Psi_{\pm}, \quad (3.36)$$

$$E(\underline{p}) = \sqrt{c^2 p^2 + m^2 c^4}$$

corresponding to "electron-like" and "positron-like" solutions, respectively. If only one of them existed,  $h_D$  would be a multiple of  $\mathbf{I}$ , and commute with all matrices.

As (3.29)  $\Rightarrow$

$$\begin{aligned} \{\underline{\alpha}, \beta\} &= 0 \Rightarrow \\ [\underline{\alpha}, \beta] &= \underline{\alpha}\beta - \beta\underline{\alpha} = -2\beta\underline{\alpha} \Rightarrow \\ [h_D, \beta] &= -2c\beta\underline{\alpha} \cdot \underline{p} \neq 0 \Rightarrow \\ \exists \beta \text{ so that } [h_d, \beta] &\neq 0 \Rightarrow h_D \neq a\mathbf{I} \Rightarrow \exists +E \text{ and } -E \end{aligned}$$

### 3.3.2 Inclusion of electromagnetic fields

Use again the minimal substitution  $\Rightarrow$

$$h_D = c\underline{\alpha} \cdot \left( \underline{p} - \frac{e}{c} \underline{A} \right) + V + \beta mc^2 \quad (3.37)$$

[In Gauss-cgs. In SI, use  $\underline{p} - e\underline{A}$ . Now  $e < 0$ .] The non-relativistic "diamagnetic" term is recovered here in 2<sup>nd</sup>-order perturbation theory with intermediate positron-like states. Using the closure,

$$\sum_n |\psi_n^-\rangle \langle \psi_n^-| = 1 \quad (3.38)$$

$$\Delta E = 2mc^2$$

we get

$$\begin{aligned} E^{(2)} &= \sum_n |\langle \psi^+ | h_D | \psi_n^- \rangle|^2 / (E^+ - E_n^-) \\ &\cong e^2 \langle \psi^+ | \underline{A}^2 | \psi^+ \rangle / 2mc^2 \end{aligned} \quad (3.39)$$

the usual diamagnetic term. (Recall that  $\frac{1}{2m}(\underline{p} - \frac{e}{c}\underline{A})^2 \rightarrow$  the term  $\frac{1}{2m}\frac{e^2}{c^2}\underline{A}^2$ .)

### 3.3.3 Free-particle solutions

In atomic units ( $e = m_e = \hbar = 4\pi\epsilon_0 = 1$ ,  $c = 137.036$ ),

$$h_D = c\underline{\alpha} \cdot \underline{p} + c^2 \beta \quad (3.40)$$

Using the Ansatz

$$\Psi = u(p) e^{i\underline{p} \cdot \underline{x}} \quad (3.41)$$

the Dirac equation  $h_D \Psi = E \Psi$  gives

$$\begin{bmatrix} -E + c^2 & 0 & cp_z & c(p_x - ip_y) \\ 0 & -E + c^2 & c(p_x + ip_y) & -cp_z \\ cp_z & c(p_x - ip_y) & -E - c^2 & 0 \\ c(p_x + ip_y) & -cp_z & 0 & -E - c^2 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix} = 0 \quad (3.42)$$

This linear, homogenous equation has solutions if  $\det [] = 0 \Rightarrow$

$$(E^2 - c^4 - c^2 p^2)^2 = 0 \quad (3.43)$$

$$E = \pm c\sqrt{(p^2 + c^2)} = \pm E_p \quad (3.44)$$

Denoting  $E_p + c^2$  by  $A$ , the spinors become ( $\sigma_z$  = the spin):

	$(E, \sigma_z)$			
$u_i$	$(E_p, \frac{1}{2})$	$(E_p, -\frac{1}{2})$	$(-E_p, \frac{1}{2})$	$(-E_p, -\frac{1}{2})$
$u_1$	1	0	$-cp_z/A$	$-c(p_x - ip_y)/A$
$u_2$	0	1	$-c(p_x + ip_y)/A$	$cp_z/A$
$u_3$	$cp_z/A$	$c(p_x - ip_y)/A$	1	0
$u_4$	$c(p_x + ip_y)/A$	$-cp_z/A$	0	1

(3.45)

The normalised spinors become

$$u(\underline{p}, E_p) = \sqrt{\frac{E_p + c^2}{2E_p}} \begin{pmatrix} 1 \cdot \binom{\alpha}{\beta} \\ \frac{c(\sigma \cdot p)}{E_p + c^2} \binom{\alpha}{\beta} \end{pmatrix} = \sqrt{\frac{E_p + c^2}{2E_p}} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \quad (3.46)$$

$$u(\underline{p}, -E_p) = \sqrt{\frac{E_p + c^2}{2E_p}} \begin{pmatrix} -c(\sigma \cdot p) \\ \frac{E_p + c^2}{1 \cdot \binom{\alpha}{\beta}} \end{pmatrix} = \sqrt{\frac{E_p + c^2}{2E_p}} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \quad (3.47)$$

where  $\binom{\alpha}{\beta}$  is either  $\binom{1}{0}$  or  $\binom{0}{1}$ .

The ratio of the norms for  $E_p > 0$ ,

$$\frac{\psi_2^2}{\psi_1^2} = \frac{c^2 p^2}{(E + c^2)^2} \cong \frac{c^2 p^2}{(2c^2)^2} = \frac{1}{4} \left( \frac{p}{mc} \right)^2 \approx \frac{1}{4} \left( \frac{v}{c} \right)^2 \quad (3.48)$$

for small  $v/c$ . Therefore  $\psi_1$  and  $\psi_2$  are called the **large** and **small components**, respectively.

For electrons in light atoms,  $v \approx 1$  a.u. and this plane-wave estimate gives

$$\frac{1}{4} \left( \frac{v}{c} \right)^2 \approx \frac{1}{4} \left( \frac{1}{137} \right)^2 \approx 10^{-5}$$

### 3.3.4 Probability density

For  $\Psi$ , satisfying

$$i\hbar \frac{\partial}{\partial t} = -i\hbar c \underline{\alpha} \cdot \nabla \Psi + \beta mc^2 \Psi \quad |\Psi^\dagger \times \quad (3.49)$$

where the Hermitian conjugate

$$\Psi^\dagger = (\psi_1^*, \psi_2^*, \psi_3^*, \psi_4^*) \quad (3.50)$$

satisfies

$$-i\hbar \frac{\partial}{\partial t} \Psi^\dagger = i\hbar c (\nabla \Psi^\dagger) \cdot \underline{\alpha} + mc^2 \Psi^\dagger \beta \quad |\times \Psi \quad (3.51)$$

Performing the two multiplications and subtracting, we get

$$i\hbar \frac{\partial}{\partial t} (\Psi^\dagger \Psi) = -i\hbar c (\Psi^\dagger \underline{\alpha} \cdot \nabla \Psi + \nabla \Psi^\dagger \cdot \underline{\alpha} \Psi) \quad (3.52)$$

$$\frac{1}{c} \frac{\partial}{\partial t} (\Psi^\dagger \Psi) + \nabla \cdot (\Psi^\dagger \underline{\alpha} \Psi) = 0 \quad (3.53)$$

Comparing with the classical continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \underline{j} = 0 \quad (3.54)$$

we identify

$$\rho = \Psi^\dagger \Psi = (\psi_1^\dagger \psi_1 + \psi_2^\dagger \psi_2 + \dots) \quad (3.55)$$

$$\underline{j} = c \Psi^\dagger \underline{\alpha} \Psi \quad (3.56)$$

From  $\underline{j} = \rho \underline{v}$ , the velocity operator (local velocity of the Dirac electron)

$$\underline{v} = c \underline{\alpha} \quad (3.57)$$

## 3.4 The Pauli limit

By substituting  $E = mc^2 + \varepsilon$ , the Dirac equation becomes

$$\begin{aligned} [c \underline{\alpha} \cdot \underline{p} + \underbrace{(\beta - 1)}_{= \begin{pmatrix} 0 & 0 \\ 0 & -2\mathbf{I} \end{pmatrix}} mc^2 + V] \Psi &= \varepsilon \Psi \quad (3.58) \end{aligned}$$

In terms of the two-spinors

$$\begin{cases} c \underline{\sigma} \cdot \underline{p} \psi_2 + V \psi_1 = \varepsilon \psi_1 \\ c \underline{\sigma} \cdot \underline{p} \psi_1 + (-2mc^2 + V) \psi_2 = \varepsilon \psi_2 \end{cases} \Rightarrow \quad (3.59)$$

$$\psi_2 = \frac{c\underline{\sigma} \cdot \underline{p}}{2mc^2 + \varepsilon - V} \psi_1 \quad (3.60)$$

$$\approx \frac{\underline{\sigma} \cdot \underline{p}}{2mc} \psi_1 \quad (3.61)$$

(Note that (3.60) is still exact.) Using the above approximation with  $\psi_1 = \psi_{\text{nr}}$ ,  $\langle \psi_1 | \psi_1 \rangle = 1 \Rightarrow$

$$\begin{aligned} \langle \Psi | \Psi \rangle &= \langle \psi_1 | \psi_1 \rangle + \langle \psi_2 | \psi_2 \rangle \\ &= 1 + \langle \psi_2 | \psi_2 \rangle \quad |\underline{p} \cdot \underline{\sigma}^\dagger \underline{\sigma} \cdot \underline{p}| = \underline{p}^2 \mathbf{I} \\ &= 1 + \frac{1}{4m^2 c^2} \langle \psi_1 | \underline{p}^2 | \psi_1 \rangle \end{aligned} \quad (3.62)$$

Then the expectation value of  $h_D$  becomes

$$\begin{aligned} \varepsilon &= \langle \Psi | h_D | \Psi \rangle / \langle \Psi | \Psi \rangle \\ &= \langle \Psi | c\underline{\alpha} \cdot \underline{p} + (\beta - 1)mc^2 + V | \Psi \rangle / \langle \Psi | \Psi \rangle \\ &= \left[ \langle \psi_1 | c\underline{\sigma} \cdot \underline{p} | \psi_2 \rangle + \langle \psi_2 | c\underline{\sigma} \cdot \underline{p} | \psi_1 \rangle - 2mc^2 \langle \psi_2 | \psi_2 \rangle \right. \\ &\quad \left. + \langle \psi_1 | V | \psi_1 \rangle + \langle \psi_2 | V | \psi_2 \rangle \right] / \left[ 1 + \langle \psi_2 | \psi_2 \rangle \right] \\ &= \left[ \frac{1}{2m} \langle \psi_1 | \underline{p}^2 | \psi_1 \rangle + \frac{1}{2m} \langle \psi_1 | \underline{p}^2 | \psi_1 \rangle - \frac{2mc^2}{4m^2 c^2} \langle \psi_1 | \underline{p}^2 | \psi_1 \rangle \right. \\ &\quad \left. + \langle \psi_1 | V | \psi_1 \rangle + \frac{1}{4m^2 c^2} \langle \psi_1 | \underline{\sigma} \cdot \underline{p} V \underline{\sigma} \cdot \underline{p} | \psi_1 \rangle \right] / \langle \Psi | \Psi \rangle \\ \varepsilon &\cong \left[ \langle \psi_1 | \frac{\underline{p}^2}{2m} | \psi_1 \rangle + \langle \psi_1 | V | \psi_1 \rangle + \frac{1}{4m^2 c^2} \langle \psi_1 | \underline{\sigma} \cdot \underline{p} V \underline{\sigma} \cdot \underline{p} | \psi_1 \rangle \right] \\ &\quad \times \left[ 1 - \frac{1}{4m^2 c^2} \langle \psi_1 | \underline{p}^2 | \psi_1 \rangle \right] + \mathcal{O}(c^{-4}) \quad \leftarrow 1/c^4 \text{ and higher order terms neglected} \\ &= \varepsilon_{\text{nr}} - \frac{1}{8m^3 c^2} \langle \psi_1 | \underline{p}^2 | \psi_1 \rangle \langle \psi_1 | \underline{p}^2 | \psi_1 \rangle \\ &\quad - \frac{1}{4m^2 c^2} \langle \psi_1 | V | \psi_1 \rangle \langle \psi_1 | \underline{p}^2 | \psi_1 \rangle \\ &\quad + \frac{1}{4m^2 c^2} \langle \psi_1 | \underline{\sigma} \cdot \underline{p} V \underline{\sigma} \cdot \underline{p} | \psi_1 \rangle + \mathcal{O}(c^{-4}) \end{aligned} \quad (3.63)$$

Trick 1:

$$\begin{aligned} \left( \frac{\underline{p}^2}{2m} + V \right) \psi_1 &= \varepsilon_{\text{nr}} \psi_1, \\ V \psi_1 &= \left( \varepsilon_{\text{nr}} - \frac{\underline{p}^2}{2m} \right) \psi_1 \end{aligned} \quad (3.64)$$

$$\begin{aligned} \varepsilon &= \varepsilon_{\text{nr}} - \frac{1}{4m^2 c^2} \varepsilon_{\text{nr}} \langle \psi_1 | \underline{p}^2 | \psi_1 \rangle \\ &\quad + \frac{1}{4m^2 c^2} \langle \psi_1 | \underline{\sigma} \cdot \underline{p} V \underline{\sigma} \cdot \underline{p} | \psi_1 \rangle \end{aligned} \quad (3.65)$$

**Trick 2:**

$$\sigma_i \sigma_j = i\delta_{ijk} \sigma_k + \delta_{ij}, \quad (3.66)$$

$$\begin{aligned} \underline{\sigma} \cdot \underline{p} V \underline{\sigma} \cdot \underline{p} &= \sigma_i p_i V \sigma_j p_j \\ &= i\delta_{ijk} \sigma_k p_i V p_j + p_k V p_k \\ &= i\delta_{ijk} \sigma_k [(p_i V) p_j + V \underbrace{p_i p_j}_{=0}] + p_k V p_k \\ &= \hbar \underline{\sigma} \cdot (\nabla V \times \underline{p}) + p_k V p_k \end{aligned} \quad (3.67)$$

[Note:  $p_i p_j = 0$  as  $i$  and  $j$  run over all combinations (summation);  $p_i p_j - p_j p_i = 0$ .]

Here

$$\begin{aligned} p_k V p_k &= \frac{1}{2} [p_k V p_k + p_k V p_k] \\ &= \frac{1}{2} [V p^2 + p^2 V] + \frac{1}{2} [(p_k V) p_k - p_k (p_k V)] \end{aligned} \quad (3.68)$$

where the first term becomes

$$\frac{1}{2} \langle \psi_1 | V p^2 + p^2 V | \psi_1 \rangle \stackrel{\text{T1}}{=} \varepsilon_{\text{nr}} \langle \psi_1 | p^2 | \psi_1 \rangle - \frac{1}{2m} \langle \psi_1 | p^4 | \psi_1 \rangle \quad (3.69)$$

and the second term becomes ( $\partial_k \equiv \frac{\partial}{\partial k}$ )

$$\begin{aligned} &\frac{1}{2} \langle \psi_1 | (p_k V) p_k - p_k (p_k V) | \psi_1 \rangle \\ &= \frac{1}{2} \langle \psi_1 | (p_k V) | p_k \psi_1 \rangle - \frac{1}{2} \langle p_k \psi_1 | (p_k V) | \psi_1 \rangle \quad | p_k = -i\hbar \partial_k \\ &= -\frac{\hbar^2}{2} \left[ \int \psi_1^* (\partial_k V) (\partial_k \psi_1) + \int (\partial_k \psi_1)^* (\partial_k V) \psi_1 \right] \\ &= -\frac{\hbar^2}{2} \left\{ \left[ \psi_1^* (\partial_k V) \psi_1 \right]_{-\infty}^{\infty} - \int (\partial_k \psi_1^*) (\partial_k V) \psi_1 - \int \psi_1^* (\partial_k^2 V) \psi_1 \right. \\ &\quad \left. + \int (\partial_k \psi_1)^* (\partial_k V) \psi_1 \right\} \\ &= \frac{1}{2} \hbar^2 \langle \psi_1 | \nabla^2 V | \psi_1 \rangle \quad | \psi(\infty) \rightarrow 0 \end{aligned} \quad (3.70)$$

Assembling the pieces in (3.65), (3.67), (3.69) and (3.70):

$$\begin{aligned} \varepsilon &= \varepsilon_{\text{nr}} - \frac{1}{4m^2 c^2} \underbrace{\varepsilon_{\text{nr}} \langle \psi_1 | p^2 | \psi_1 \rangle}_{+ \frac{1}{4m^2 c^2} \left[ \langle \psi_1 | \hbar \underline{\sigma} \cdot (\nabla V \times \underline{p}) | \psi_1 \rangle \right.} \\ &\quad \left. + \varepsilon_{\text{nr}} \langle \psi_1 | p^2 | \psi_1 \rangle - \frac{1}{2m} \langle \psi_1 | p^4 | \psi_1 \rangle \right. \\ &\quad \left. + \frac{1}{2} \hbar^2 \langle \psi_1 | \nabla^2 V | \psi_1 \rangle \right]} \\ &= \varepsilon_{\text{nr}} + \langle h_m + h_{\text{SO}} + h_{\text{d}} \rangle + \mathcal{O}(c^{-4}) \end{aligned} \quad (3.71)$$

$$\begin{cases} \langle h_m \rangle = -\frac{1}{8m^3c^2} \langle \psi_1 | p^4 | \psi_1 \rangle & \text{(mass-velocity)} \\ \langle h_{SO} \rangle = \frac{\hbar}{4m^2c^2} \langle \psi_1 | \underline{\sigma} \cdot (\nabla V \times \underline{p}) | \psi_1 \rangle & \text{(spin-orbit)} \\ \langle h_d \rangle = \frac{\hbar^2}{8m^2c^2} \langle \psi_1 | \nabla^2 V | \psi_1 \rangle & \text{(Darwin)} \end{cases} \quad (3.72)$$

Returning to (3.65), in terms of  $\psi_2$ ,

$$\varepsilon \cong \varepsilon_{nr} - \varepsilon_{nr} + \langle \psi_2 | V | \psi_2 \rangle \quad (3.73)$$

For the Coulomb potential of a point charge  $Z$ ,

$$\nabla^2 V = -Z \nabla^2 \left( \frac{1}{r} \right) = 4\pi Z \underbrace{\delta(\underline{r})}_{\text{3-D } \delta\text{-func}} \Rightarrow \quad (3.74)$$

$$\begin{aligned} \langle h_d \rangle &= \frac{\hbar^2}{8m^2c^2} \langle \psi_1 | (4\pi Z) \delta(\underline{r}) | \psi_1 \rangle \\ &= \frac{\pi \hbar^2 Z}{2m^2c^2} |\psi_1(0)|^2 \end{aligned} \quad (3.75)$$

**Example 1:** For the 1s state of a hydrogenic atom, in a.u.,

$$\psi_{1s} = \sqrt{\frac{Z^3}{\pi}} e^{-Zr},$$

$$\begin{aligned} \langle h_d \rangle &= \frac{\pi Z}{2c^2} \frac{Z^3}{\pi} = \frac{Z^4}{2c^2} \\ \langle h_m \rangle &= -\frac{1}{8m^3c^2} \langle p^4 \rangle = -\frac{1}{2mc^2} \langle \left( \frac{p^2}{2m} \right)^2 \rangle \\ &= -\frac{1}{2mc^2} \langle (E - V)^2 \rangle \\ &= -\frac{1}{2mc^2} \left[ \left( \frac{Z^2}{2} \right)^2 - 2 \left( -\frac{Z^2}{2} \right) \langle V \rangle + \langle V^2 \rangle \right] \end{aligned}$$

As

$$\begin{aligned} \langle V \rangle &= \frac{Z^3}{\pi} (4\pi) \int_0^\infty e^{-2Zr} \left( \frac{-Z}{r} \right) r^2 dr \\ &= -4Z^4 \int_0^\infty e^{-2Zr} r dr = (-4Z^4) \frac{1!}{(2Z)^2} = -Z^2, \\ \langle V^2 \rangle &= +4Z^3 \int_0^\infty e^{-2Zr} \left( \frac{Z}{r} \right)^2 r^2 dr = 4Z^5 \frac{0!}{2Z} = 2Z^4, \\ \langle h_m \rangle &= -\frac{1}{2mc^2} Z^4 \left[ \frac{1}{4} - 1 + 2 \right] = -\frac{5}{8c^2} Z^4 \\ \langle h_{SO} \rangle &= 0 \end{aligned}$$

Summing up,

$$E_{\text{rel}} = \langle h_m + h_d \rangle = \frac{Z^4}{c^2} \left( -\frac{5}{8} + \frac{4}{8} \right) = -\frac{Z^4}{8c^2} \quad (3.76)$$

### 3.5 Central fields

We now return to the full Dirac equation with a local potential  $V(\underline{r}) = V(r)$ . As

$$[\underline{l}, h_D] = i c \underline{\alpha} \times \underline{p} \neq 0 \quad (3.77)$$

$$[\underline{s}, h_D] = -i c \underline{\alpha} \times \underline{p} \neq 0 \quad (3.78)$$

neither  $\underline{l}$  or  $\underline{s}$  can have simultaneous eigenstates with  $h_D$  but their sum

$$\underline{j} = \underline{l} + \underline{s} \quad (3.79)$$

can because

$$[\underline{j}, h_D] = 0 \quad (3.80)$$

#### Details:

$$\begin{aligned} \underline{l} &= \underline{r} \times \underline{p} \\ [\underline{l}, \beta] &= 0, \quad [\underline{l}, V] = 0, \quad [\underline{l}, \underline{\alpha} \cdot \underline{p}] \neq 0 \end{aligned}$$

Consider the component  $l_1$ :

$$\begin{aligned} [l_1, \underline{\alpha} \cdot \underline{p}] &= \alpha_1 \underbrace{[l_1, p_1]}_{=0} + \alpha_2 [l_1, p_2] + \alpha_3 [l_1, p_3] \\ \underline{l} &= \underline{r} \times \underline{p} = -i \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ \partial_x & \partial_y & \partial_z \end{vmatrix} \Rightarrow l_1 = -i(y\partial_z - z\partial_y) \end{aligned}$$

$$\begin{aligned} [l_1, p_2] &= (-i)^2 [y\partial_z - z\partial_y, \partial_y] \\ &= - \left( \underbrace{y \frac{\partial^2}{\partial y \partial z}}_{\text{cycl.}} \underbrace{-z \frac{\partial^2}{\partial y^2}}_{\text{cycl.}} - \partial_z \underbrace{-y \frac{\partial^2}{\partial y \partial z}}_{\text{cycl.}} \underbrace{+z \frac{\partial^2}{\partial y^2}}_{\text{cycl.}} \right) \\ &= \frac{\partial}{\partial z} = ip_3, \text{ cycl.} \Rightarrow \\ [l_1, \underline{\alpha} \cdot \underline{p}] &= \alpha_2 ip_3 - \alpha_3 ip_2 = i(\underline{\alpha} \times \underline{p})_1, \text{ cycl.} \Rightarrow \\ [l, \underline{\alpha} \cdot \underline{p}] &= i \underline{\alpha} \times \underline{p} \quad \square \end{aligned}$$

Similarly for  $[\underline{\sigma}, \underline{\alpha} \cdot \underline{p}]$  (=with spin),

$$\begin{aligned} [\sigma_1, \underline{\alpha} \cdot \underline{p}] &= \begin{pmatrix} \sigma_1 & 0 \\ 0 & \sigma_1 \end{pmatrix} \begin{pmatrix} 0 & \underline{\sigma} \cdot \underline{p} \\ \underline{\sigma} \cdot \underline{p} & 0 \end{pmatrix} - \begin{pmatrix} 0 & \underline{\sigma} \cdot \underline{p} \\ \underline{\sigma} \cdot \underline{p} & 0 \end{pmatrix} \begin{pmatrix} \delta_1 & 0 \\ 0 & \delta_1 \end{pmatrix} \\ &= \begin{pmatrix} 0 & \sigma_1 \underline{\sigma} \cdot \underline{p} \\ \sigma_1 \underline{\sigma} \cdot \underline{p} & 0 \end{pmatrix} - \begin{pmatrix} 0 & \underline{\sigma} \cdot \underline{p} \sigma_1 \\ \underline{\sigma} \cdot \underline{p} \sigma_1 & 0 \end{pmatrix} \\ &= \begin{pmatrix} 0 & [\sigma_1, \underline{\sigma} \cdot \underline{p}] \\ [\sigma_1, \underline{\sigma} \cdot \underline{p}] & 0 \end{pmatrix} \end{aligned}$$

As  $[\sigma_1, \sigma_2] = 2i\sigma_3$ , cycl.,

$$\begin{aligned} [\sigma_1, \underline{\sigma} \cdot \underline{p}] &= \sigma_1(\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3) \\ &\quad - (\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3) \sigma_1 \\ &= p_1 + \sigma_1 \sigma_2 p_2 + \sigma_1 \sigma_3 p_3 \\ &\quad - p_1 - \sigma_2 \sigma_1 p_2 - \sigma_3 \sigma_1 p_3 \\ &= \underbrace{[\sigma_1, \sigma_2]}_{2i\sigma_3} p_2 - \underbrace{[\sigma_3, \sigma_1]}_{2i\sigma_2} p_3 \\ &= 2i[\sigma_3 p_2 - \sigma_2 p_3] = 2i(p_2 \sigma_3 - p_3 \sigma_2) \\ &= 2i(\underline{p} \times \underline{\sigma}), \text{ cycl.} \Rightarrow \\ [\underline{\sigma}, \underline{\alpha} \cdot \underline{p}] &= 2i\underline{p} \times \underline{\alpha} = -2i\underline{\alpha} \times \underline{p} \quad \square \end{aligned}$$

Define

$$\underline{s} = \frac{1}{2}\hbar\underline{\sigma} \quad (3.81)$$

$\Rightarrow (3.79)$

As a further detail, consider the operator

$$K = (V\sigma \cdot \underline{l} + 1)\beta \quad (3.82)$$

We shall show that

$$[K, \underline{j}] = 0 \quad (3.83)$$

$$[K, h_D] = 0 \quad (3.84)$$

In other words,  $K$ ,  $h_D$ ,  $\underline{j}^2$  and  $j_z$  can have simultaneous eigenstates.

**Theorem a:**

For two vectors  $\underline{A}$  and  $\underline{B}$  which commute with  $\underline{\sigma}$  but not necessarily with each other,

$$(\underline{\sigma} \cdot \underline{A})(\underline{\sigma} \cdot \underline{B}) = \underline{A} \cdot \underline{B} + i\underline{\sigma} \cdot (\underline{A} \times \underline{B}) \quad (3.85)$$

**Proof:**

The  $\underline{\sigma}$  matrices simultaneously satisfy

$$\left. \begin{aligned} [\sigma_i, \sigma_k] &= \sigma_i \sigma_k - \sigma_k \sigma_i = 2i\delta_{ikl}\delta_l \\ \{\sigma_i, \sigma_k\} &= \sigma_i \sigma_k + \sigma_k \sigma_i = 2\delta_{ik} \end{aligned} \right\} \Rightarrow$$

$$\sigma_i^2 = 1 \quad (i = k) \quad (3.86)$$

$$\sigma_i \sigma_k = i\delta_{ikl}\sigma_l \quad (i \neq k) \quad (3.87)$$

$$\begin{aligned} (\underline{\sigma} \cdot \underline{A})(\underline{\sigma} \cdot \underline{B}) &= \sigma_i A_i \sigma_j B_j \\ &\stackrel{[\underline{\sigma}, \underline{A}]=0}{=} \underbrace{\sigma_i \sigma_i}_{=1} A_i B_i + \sum_{i \neq j} \sigma_i \sigma_j A_i B_j \\ &= \underline{A} \cdot \underline{B} + \sum_{i < j} \underbrace{\sigma_i \sigma_j}_{i\delta_{ijk}\delta_k} \underbrace{(A_i B_j - A_j B_i)}_{(\underline{A} \times \underline{B})_k} \\ &= \underline{A} \cdot \underline{B} + i\underline{\sigma} \cdot \underline{A} \times \underline{B} \quad \square \end{aligned} \quad (3.88)$$

The equation holds for both two- and four-component  $\underline{\sigma}$

**Theorem b:**

$$(\underline{\alpha} \cdot \underline{A})(\underline{\alpha} \cdot \underline{B}) = (\underline{\sigma} \cdot \underline{A})(\underline{\sigma} \cdot \underline{B}) \quad (3.89)$$

**Proof:**

$$\begin{aligned} \begin{pmatrix} 0 & \underline{\sigma} \cdot \underline{A} \\ \underline{\sigma} \cdot \underline{A} & 0 \end{pmatrix} \begin{pmatrix} 0 & \underline{\sigma} \cdot \underline{B} \\ \underline{\sigma} \cdot \underline{B} & 0 \end{pmatrix} &= \begin{pmatrix} \underline{\sigma} \cdot \underline{A} \underline{\sigma} \cdot \underline{B} & 0 \\ 0 & \underline{\sigma} \cdot \underline{A} \underline{\sigma} \cdot \underline{B} \end{pmatrix} \\ &= (\underline{\sigma}^4 \cdot \underline{A})(\underline{\sigma}^4 \cdot \underline{B}) \quad \square \end{aligned}$$

$\underline{\sigma}^4$  denotes a four dimensional  $\sigma$ .

**Theorem c:**

$$(\underline{\alpha} \cdot \underline{A})(\underline{\alpha} \cdot \underline{B}) = -\gamma_5 \underline{A} \cdot \underline{B} + i\underline{\alpha} \cdot (\underline{A} \times \underline{B}), \quad (3.90)$$

where

$$\gamma_5 = \gamma_1 \gamma_2 \gamma_3 \gamma_4. \quad (3.91)$$

**Proof:**

We use the representation

$$\underline{\gamma} = i\underline{\alpha}\beta = \begin{pmatrix} 0 & -i\underline{\sigma} \\ i\underline{\sigma} & 0 \end{pmatrix}$$

$$\gamma_5 = \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Then, recalling that  $i^3 = -i$ ,

$$\begin{aligned} \gamma_5 &= -i \underbrace{\begin{pmatrix} 0 & -\sigma_1 \\ \sigma_1 & 0 \end{pmatrix}}_{\sigma_1} \underbrace{\begin{pmatrix} 0 & -\sigma_2 \\ \sigma_2 & 0 \end{pmatrix}}_{\sigma_2} \underbrace{\begin{pmatrix} 0 & -\sigma_3 \\ \sigma_3 & 0 \end{pmatrix}}_{\sigma_3} \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}_{\beta} \\ &= -i \begin{pmatrix} -\sigma_1\sigma_2 & 0 \\ 0 & -\sigma_1\sigma_2 \end{pmatrix} \begin{pmatrix} 0 & \sigma_3 \\ \sigma_3 & 0 \end{pmatrix} \\ &= i \begin{pmatrix} 0 & \sigma_1\sigma_2\sigma_3 \\ \sigma_1\sigma_2\sigma_3 & 0 \end{pmatrix} \quad \left| \sigma_1\sigma_2 = i\sigma_3 \right. \\ &= - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \end{aligned} \tag{3.92}$$

Then

$$\begin{cases} \gamma_5\underline{\alpha} = - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} = - \begin{pmatrix} \underline{\sigma} & 0 \\ 0 & \underline{\sigma} \end{pmatrix} = -\underline{\sigma}^4 \\ \underline{\alpha}\gamma_5 = - \begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = - \begin{pmatrix} \underline{\sigma} & 0 \\ 0 & \underline{\sigma} \end{pmatrix} = -\underline{\sigma}^4, \end{cases} \tag{3.93}$$

$$\begin{cases} \gamma_5\underline{\sigma}^4 = - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \underline{\sigma} & 0 \\ 0 & \underline{\sigma} \end{pmatrix} = - \begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} = -\underline{\alpha} \\ \underline{\sigma}^4\gamma_5 = - \begin{pmatrix} \underline{\sigma} & 0 \\ 0 & \underline{\sigma} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = - \begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} = -\underline{\alpha}. \end{cases} \tag{3.94}$$

Multiplying **Theorem a**, (3.85), from left by  $-\gamma_5$ :

$$(-\underbrace{\gamma_5\underline{\sigma}^4}_{-\underline{\alpha}} \cdot \underline{A})(\underline{\sigma} \cdot \underline{B}) = -\gamma_5 \underline{A} \cdot \underline{B} + i(-\underbrace{\gamma_5\underline{\sigma}^4}_{\underline{\alpha}}) \cdot \underline{A} \times \underline{B} \quad \square$$

**Theorem d:**

Because

$$\begin{aligned} \underline{l} &= \underline{r} \times \underline{p} \quad (\perp \underline{p}), \\ \underline{p} \cdot \underline{l} &= \underline{l} \cdot \underline{p} = 0. \end{aligned} \tag{3.95}$$

Furthermore,

$$\underline{l} \times \underline{p} + \underline{p} \times \underline{l} = 2i\underline{p} \tag{3.96}$$

**Proof:**

$$\underline{A} \times \underline{B} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix}$$

$$\underline{A} \times \underline{B} + \underline{B} \times \underline{A} = \hat{i}([A_y, B_z] - [A_z, B_y]) + \hat{j}(-[A_z, B_x] + [A_x, B_z]) + \hat{k}([A_x, B_y] - [A_y, B_x])$$

$$\begin{aligned} (\underline{l} \times \underline{p} + \underline{p} \times \underline{l})_x &= [l_y, p_z] - [l_z, p_y] \\ &= -[(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z})(\frac{\partial}{\partial z}) - (\frac{\partial}{\partial z})(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z})] \\ &\quad + [(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})(\frac{\partial}{\partial y}) - (\frac{\partial}{\partial y})(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})] \\ &= \frac{\partial}{\partial x} + \frac{\partial}{\partial x} = 2ip_x, \quad \text{cycl.} \square \end{aligned}$$

Then the anticommutator

$$\begin{aligned} \{\underline{\sigma} \cdot \underline{l}, \underline{\alpha} \cdot \underline{p}\} &= (\underline{\sigma} \cdot \underline{l})(\underline{\alpha} \cdot \underline{p}) + (\underline{\alpha} \cdot \underline{p})(\underline{\sigma} \cdot \underline{l}) \\ &\stackrel{(3.90)}{=} -\gamma_5 \underbrace{[\underline{l} \cdot \underline{p}]}_{=0} + \underbrace{\underline{p} \cdot \underline{l}}_{=0} + i\underbrace{\underline{\sigma}^4 \cdot (\underline{l} \times \underline{p} + \underline{p} \times \underline{l})}_{2ip} \\ &= -2\underline{\alpha} \cdot \underline{p} \end{aligned} \tag{3.97}$$

**Theorem e:**

$$[K, \underline{\alpha} \cdot \underline{p}] = [\beta \underline{\sigma} \cdot \underline{l}, \underline{\alpha} \cdot \underline{p}] + [\beta, \underline{\alpha} \cdot \underline{p}]$$

Because

$$\begin{aligned} -\underline{\alpha} \beta &= \beta \underline{\alpha}, \\ -\underline{\alpha} \cdot \underline{p} \beta \underline{\sigma} \cdot \underline{l} &= \beta (\underline{\alpha} \cdot \underline{p}) \underline{\sigma} \cdot \underline{l} \Rightarrow \\ [K, \underline{\alpha} \cdot \underline{p}] &= \beta \underbrace{\{\underline{\sigma} \cdot \underline{l}, \underline{\alpha} \cdot \underline{p}\}}_{-2\underline{\alpha} \cdot \underline{p}} + 2\beta \underline{\alpha} \cdot \underline{p} = 0 \end{aligned} \tag{3.98}$$

**Theorem f:**

As

$$[\beta, \beta] = 0, \quad [K, \beta] = 0. \tag{3.99}$$

Theorem *e+f*  $\Rightarrow$

$$[K, h_D] = 0 \quad (3.100)$$

It remains to show that  $[K, \underline{j}] = 0$ .

**Theorem *g*:**

From theorem *a*, (3.85), taking  $\underline{B}$  as an arbitrary vector, commuting with  $\underline{A}$ ,

$$(\underline{\sigma} \cdot \underline{A})\underline{\sigma} = \underline{A} + i\underline{\sigma} \times \underline{A}, \quad (3.101)$$

where we used

$$\underline{\sigma} \cdot \underline{A} \times \underline{B} = \underline{\sigma} \times \underline{A} \cdot \underline{B}.$$

Similarly, letting  $\underline{A}$  be arbitrary,

$$\underline{\sigma}(\underline{\sigma} \cdot \underline{B}) = \underline{B} + i\underline{B} \times \underline{\sigma}. \quad (3.102)$$

Letting then  $\underline{A} = \underline{B} = \underline{l}$  and subtracting (3.101)-(3.102),

$$\begin{aligned} [\underline{\sigma} \cdot \underline{l}, \underline{\sigma}] &= i\underline{\sigma} \times \underline{l} - i\underline{l} \times \underline{\sigma} \\ &= 2i\underline{\sigma} \times \underline{l} \end{aligned} \quad (3.103)$$

**Theorem *h*:**

Let  $\underline{A}$  commute with  $\underline{l}$ . Then

$$\begin{aligned} [\underline{A} \cdot \underline{l}, \underline{l}] &= \sum_{i=1}^3 \sum_{j=1}^3 [A_i l_i l_j \hat{x}_j - l_j \hat{x}_j A_i l_i] \\ &= \sum_{i,j} A_i \hat{x}_j \underbrace{[l_i l_j - l_j l_i]}_{\delta_{ijk} i l_k = -i \delta_{jik} l_k} \\ &= -i \underline{A} \times \underline{l} \end{aligned} \quad (3.104)$$

Letting  $\underline{A} = \underline{\sigma}$ ,

$$[\underline{\sigma} \cdot \underline{l}, \underline{l}] = -i\underline{\sigma} \times \underline{l} \quad (3.105)$$

**Theorem *i*:**

The desired commutator (note:  $[K, \beta] = 0$ )

$$\begin{aligned} [K, \underline{j}] &= [\beta \underline{\sigma} \cdot \underline{l}, \underline{l} + \frac{1}{2} \underline{\sigma}] \\ &= \beta [\underline{\sigma} \cdot \underline{l}, \underline{l}] + \frac{1}{2} \beta [\underline{\sigma} \cdot \underline{l}, \underline{\sigma}] \\ &= \beta (-i \underline{\sigma} \times \underline{l}) + \frac{1}{2} \beta (2i \underline{\sigma} \times \underline{l}) = 0 \quad \square \end{aligned} \quad (3.106)$$

Summarizing,

$$[K, \underline{j}] = [K, h_D] = [\underline{j}, h_D] = 0 \quad (3.107)$$

Denote the eigenvalues of  $K$  by  $-\kappa$ :

$$K\chi_\kappa^m = -\kappa\chi_\kappa^m, \quad (3.108)$$

where the  $\underline{\sigma}$  (in  $K$ ) are 2-component ones, and the 2-component spinors

$$\chi_\kappa^m \equiv |lsjm\rangle \quad (3.109)$$

The quantum number  $\kappa$  carries both  $j$  and  $l$ :

$$\kappa = \begin{cases} -l-1, & j = l + \frac{1}{2} \quad (\text{state } 'l') \\ l, & j = l - \frac{1}{2} \quad (\text{state } 'l^* \text{ or } 'l\bar{l}). \end{cases} \quad (3.110)$$

The lowest values are

$$\begin{array}{cccccccccc} \kappa & = & -1 & 1 & -2 & 2 & -3 & 3 & -4 & \dots \\ s_{1/2} & & p_{1/2} & p_{3/2} & d_{3/2} & d_{5/2} & f_{5/2} & f_{7/2} & \dots \\ \text{s} & & \text{p}^* & \text{p} & \text{d}^* & \text{d} & \text{f}^* & \text{f} & \dots \end{array} \quad (3.111)$$

From

$$\begin{aligned} \underline{j} &= \underline{l} + \underline{s}, \\ \underline{j}^2 &= \underline{l}^2 + 2\underline{l} \cdot \underline{s} + \underline{s}^2 \Rightarrow \\ \underline{l} \cdot \underline{s} &\equiv \frac{1}{2}[\underline{j}^2 - \underline{l}^2 - \underline{s}^2] \end{aligned} \quad (3.112)$$

Consequently

$$\begin{aligned} K &= \underline{\sigma} \cdot \underline{l} + 1 \\ &= \underline{j}^2 - \underline{l}^2 - \underline{s}^2 + 1 \\ K\chi_\kappa^m &= K|lsjm\rangle = [j(j+1) - l(l+1) - \underbrace{s(s+1)}_{\frac{3}{4}} + 1]\chi_\kappa^m \\ &= [(j + \frac{1}{2})^2 - l(l+1)]\chi_\kappa^m \\ &= -\kappa\chi_\kappa^m, \end{aligned}$$

whence

$$\kappa = l(l+1) - (j + \frac{1}{2})^2, \quad (3.113)$$

as can be verified from Table (3.111).

For the 4-component case we introduce the Ansatz

$$\Psi = \Psi_\kappa^m = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} g(r)\chi_\kappa^m \\ i f(r)\chi_{-\kappa}^m \end{pmatrix} = \frac{1}{r} \begin{pmatrix} P(r)\chi_\kappa^m \\ i Q(r)\chi_{-\kappa}^m \end{pmatrix} \quad (3.114)$$

for which, indeed

$$K\Psi_\kappa^m = \begin{pmatrix} \underline{\sigma} \cdot \underline{l} + 1 & 0 \\ 0 & -\underline{\sigma} \cdot \underline{l} - 1 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = -\kappa \Psi_\kappa^m. \quad (3.115)$$

This  $\Psi$  is an eigenfunction to  $h_D, K, \underline{j}^2$  and  $j_z$ .

### 3.5.1 The radial Part

From

$$\begin{aligned} \underline{A} \times (\underline{B} \times \underline{C}) &= (\underline{A} \cdot \underline{C})\underline{B} - (\underline{A} \cdot \underline{B})\underline{C}, \\ (\underline{A} \cdot \underline{B})\underline{C} &= (\underline{A} \cdot \underline{C})\underline{B} - \underline{A} \times (\underline{B} \times \underline{C}), \end{aligned} \quad (3.116)$$

with

$$\begin{aligned} \underline{A} &= \underline{B} = \hat{\underline{r}} = (\hat{i}, \hat{j}, \hat{k}), \quad \underline{C} = \nabla, \\ \nabla &= \hat{\underline{r}}(\hat{r} \cdot \nabla) - \hat{\underline{r}} \times (\hat{\underline{r}} \times \nabla) \\ &= \hat{e}_r \frac{\partial}{\partial r} - i \frac{\hat{e}_r}{r} \times \underline{l}. \end{aligned} \quad (3.117)$$

Here  $\hat{e}_r$  is the unit vector along the radius (and  $\underline{l} = \underline{r} \times \underline{p}$ ). Consequently the kinetic energy term

$$\underline{\alpha} \cdot \underline{p} = -i\alpha_r \frac{\partial}{\partial r} - \frac{1}{r} \underline{\alpha} \cdot \hat{\underline{r}} \times \underline{l}. \quad (3.118)$$

Denoting

$$\underline{\sigma} = \underline{\sigma}^4 = \begin{pmatrix} \underline{\sigma} & 0 \\ 0 & \underline{\sigma} \end{pmatrix}$$

and using

$$\underline{\alpha} \cdot \underline{A} \underline{\alpha} \cdot \underline{B} = \underline{A} \cdot \underline{B} + i\underline{\alpha} \cdot \underline{A} \times \underline{B} \quad [3.88-3.89]$$

for  $\underline{A} = \hat{\underline{r}}$  and  $\underline{B} = \underline{l}$ ,

$$\underbrace{(\underline{\alpha} \cdot \hat{\underline{r}})(\underline{\alpha} \cdot \underline{l})}_{\alpha_r} = \underbrace{\hat{\underline{r}} \cdot \underline{l}}_{=0} + i\underline{\alpha} \cdot \hat{\underline{r}} \times \underline{l} \quad (3.119)$$

( $\hat{\underline{r}} \cdot \underline{l} = 0$  as the angular momentum has no radial components.) Multiplying by  $i\gamma_5$  and recalling that  $\underline{\alpha} = -\gamma_5 \underline{\sigma}$ ,

$$\begin{aligned} i\gamma_5 \alpha_r (\underline{\alpha} \cdot \underline{l}) &= -\gamma_5 \underline{\sigma} \cdot \underline{r} \times \underline{l} \\ i\gamma_5 \sigma_r (\underline{\sigma} \cdot \underline{l}) &= \underline{\alpha} \cdot \underline{r} \times \underline{l}. \end{aligned} \quad (3.120)$$

$$\begin{aligned}
\underline{\alpha} \cdot \underline{p} &= i\gamma_5 \sigma_r \frac{\partial}{\partial r} - \frac{1}{r} i\gamma_5 \sigma_r (\underline{\alpha} \cdot \underline{l}) \\
&= i\gamma_5 \sigma_r \left[ \frac{\partial}{\partial r} - \frac{1}{r} \underline{\alpha} \cdot \underline{l} \right].
\end{aligned} \tag{3.121}$$

Thus the Dirac Hamiltonian

$$\begin{aligned}
h_D &= c\underline{\alpha} \cdot \underline{p} + \beta mc^2 + V(r) \\
&= i\gamma_5 \sigma_r \left[ \frac{\partial}{\partial r} - \frac{1}{r} \underline{\alpha} \cdot \underline{l} \right] + \beta mc^2 + V(r).
\end{aligned} \tag{3.122}$$

with

$$\begin{aligned}
K &= \beta(\underline{\alpha} \cdot \underline{l} + 1), \quad \beta^2 = 1 \Rightarrow \\
\underline{\alpha} \cdot \underline{l} &= \beta K - 1,
\end{aligned} \tag{3.123}$$

$$h_D = i\gamma_5 \sigma_r \left[ \frac{\partial}{\partial r} + \frac{1}{r} - \frac{\beta K}{r} \right] + \beta mc^2 + V(r)$$

$$(3.124)$$

**Theorem a:**

$$\sigma_r^2 = 1 \tag{3.125}$$

(like in the cartesian case,  $\sigma_i^2 = 1$ )

**Proof:**

$$\begin{aligned}
\sigma_r &= \underline{\alpha} \cdot \hat{r} = \sum_i \sigma_i \frac{1}{r} (\sigma_x x + \sigma_y y + \sigma_z z) \\
\sigma_r^2 &= \frac{1}{r^2} \left[ \sum_i \sigma_i^2 x_i^2 + \sum_{i>j} x_i x_j \underbrace{(\sigma_i \sigma_j + \sigma_j \sigma_i)}_{=0} \right] = 1 \quad \square
\end{aligned}$$

**Theorem b:**

$$\{K, \sigma_r\} = 0 \tag{3.126}$$

**Proof:**

$$\begin{aligned}
K &= \beta(\underline{\alpha} \cdot \underline{l} + 1) \\
[\beta, \underline{\alpha} \cdot \underline{l}] &= 0 \\
[\beta, \sigma_r] &= 0
\end{aligned}$$

(3.85)  $\Rightarrow$

$$\left. \begin{aligned} (\underline{\sigma} \cdot \underline{l})(\underline{\sigma} \cdot \hat{\underline{r}}) &= \underline{l} \cdot \hat{\underline{r}} + i\underline{\sigma} \cdot (\underline{l} \times \hat{\underline{r}}) \\ (\underline{\sigma} \cdot \hat{\underline{r}})(\underline{\sigma} \cdot \underline{l}) &= \hat{\underline{r}} \cdot \underline{l} + i\underline{\sigma} \cdot (\hat{\underline{r}} \times \underline{l}) \end{aligned} \right\} \Rightarrow$$

$$\begin{aligned} \{K, \sigma_r\} &= \{\beta(\underline{\sigma} \cdot \underline{l} + 1), \underline{\sigma} \cdot \hat{\underline{r}}\} \\ &= \beta i \underline{\sigma} \cdot \underbrace{(\underline{l} \times \hat{\underline{r}} + \hat{\underline{r}} \times \underline{l})}_{2i\underline{l}} + 2\beta \underline{\sigma} \cdot \hat{\underline{r}} \\ &= 0 \quad \square \end{aligned}$$

**Theorem c:**

$$\sigma_r \chi_\kappa^m = -\chi_{-\kappa}^m \quad (3.127)$$

**Proof:**

$$\begin{aligned} K(\sigma_r \chi_\kappa^m) &= -\sigma_r(K \chi_\kappa^m) \\ &= \kappa(\sigma_r \chi_\kappa^m) \end{aligned} \quad (3.128)$$

Thus the eigenvalue of  $\sigma_r \chi_\kappa^m$  is  $\kappa$ , while

$$K \chi_\kappa^m = -\kappa \chi_\kappa^m \quad [3.108]$$

whence

$$\sigma_r \chi_\kappa^m = -\chi_{-\kappa}^m \quad \square$$

Recalling now that

$$\gamma_5 = -\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

(3.124) becomes

$$\left[ i c(-) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \sigma_r \left( \frac{\partial}{\partial r} + \frac{1}{r} - \frac{1}{r} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} K^4 \right) + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} m c^2 + V - E \right] \begin{pmatrix} g \chi_\kappa^m \\ i f \chi_{-\kappa}^m \end{pmatrix} = 0.$$

where  $K^4$  denotes the four-dimensional K-operator. Recalling

$$K^4 \begin{pmatrix} g \chi_\kappa \\ i f \chi_{-\kappa} \end{pmatrix} = (-\kappa) \begin{pmatrix} g \chi_\kappa \\ i f \chi_{-\kappa} \end{pmatrix},$$

$$\begin{aligned}
& -ic \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \sigma_r \left[ \left( \frac{\partial}{\partial r} + \frac{1}{r} \right) \begin{pmatrix} g\chi_\kappa \\ if\chi_{-\kappa} \end{pmatrix} - \frac{1}{r} \begin{pmatrix} g\chi_\kappa \\ if\chi_{-\kappa} \end{pmatrix} \right] \\
& + mc^2 \begin{pmatrix} g\chi_\kappa \\ -if\chi_{-\kappa} \end{pmatrix} + (V - E) \begin{pmatrix} g\chi_\kappa \\ if\chi_{-\kappa} \end{pmatrix} = 0.
\end{aligned}$$

Then operate with  $\sigma_r$  using (3.127):

$$\begin{aligned}
& -ic \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \left[ - \left( \frac{\partial}{\partial r} + \frac{1}{r} \right) \begin{pmatrix} g\chi_\kappa \\ if\chi_{-\kappa} \end{pmatrix} + \frac{1}{r} \begin{pmatrix} g\chi_{-\kappa} \\ if\chi_\kappa \end{pmatrix} \right] \\
& + mc^2 \begin{pmatrix} g\chi_\kappa \\ -if\chi_{-\kappa} \end{pmatrix} + (V - E) \begin{pmatrix} g\chi_\kappa \\ if\chi_{-\kappa} \end{pmatrix} = 0, \\
& ic \left( \frac{\partial}{\partial r} + \frac{1}{r} \right) \begin{pmatrix} if\chi_\kappa \\ g\chi_{-\kappa} \end{pmatrix} - \frac{ic}{r} \begin{pmatrix} if\kappa\chi_\kappa \\ -g\kappa\chi_{-\kappa} \end{pmatrix} \\
& + mc^2 \begin{pmatrix} g\chi_\kappa \\ -if\chi_{-\kappa} \end{pmatrix} + (V - E) \begin{pmatrix} g\chi_\kappa \\ if\chi_{-\kappa} \end{pmatrix} = 0.
\end{aligned}$$

For the two components

$$ic \left( \frac{\partial}{\partial r} + (1\{\mp\}\kappa) \frac{1}{r} \right) \begin{pmatrix} if\chi_\kappa \\ g\chi_{-\kappa} \end{pmatrix} + [\{\pm\}mc^2 + V - E] \begin{pmatrix} g\chi_\kappa \\ if\chi_{-\kappa} \end{pmatrix} = 0 \quad (3.129)$$

Dividing by the angular part and  $i$  we get

$$\begin{cases} -c \left( \frac{\partial}{\partial r} + \frac{1-\kappa}{r} \right) f + (mc^2 + V - E) g = 0 \\ c \left( \frac{\partial}{\partial r} + \frac{1+\kappa}{r} \right) g + (-mc^2 + V - E) f = 0 \end{cases} \quad (3.130)$$

Introducing

$$\begin{cases} P = rg \\ Q = rf \end{cases}, \quad (3.131)$$

$$\begin{cases} \frac{dP}{dr} = g + r \frac{dg}{dr} \\ \frac{dQ}{dr} = f + r \frac{df}{dr} \end{cases} \Rightarrow \begin{cases} \frac{dg}{dr} = \frac{1}{r} \frac{dP}{dr} - \frac{P}{r^2} \\ \frac{df}{dr} = \frac{1}{r} \frac{dQ}{dr} - \frac{Q}{r^2} \end{cases} \quad (3.132)$$

$$\begin{cases} \frac{1}{r} \left( \frac{dQ}{dr} - \frac{Q}{r} + (1-\kappa) \frac{Q}{r} \right) + \left( -mc + \frac{E-V}{c} \right) \frac{P}{r} = 0 \\ \frac{1}{r} \left( \frac{dP}{dr} - \frac{P}{r} + (1+\kappa) \frac{P}{r} \right) + \left( -mc + \frac{V-E}{c} \right) \frac{Q}{r} = 0 \end{cases} \quad (3.133)$$

$$\begin{cases} \frac{dP}{dr} + \kappa \frac{P}{r} + \left( -mc + \frac{V - E}{c} \right) Q = 0 \\ \frac{dQ}{dr} - \kappa \frac{Q}{r} + \left( -mc + \frac{E - V}{c} \right) P = 0 \end{cases} \quad (3.134)$$

### 3.5.2 Non-relativistic limit

Let the potential  $|V| \ll E \approx mc^2$ . For the  $E > 0$  states

$$-mc + \frac{V - E}{c} \approx -2mc \Rightarrow Q \approx \frac{1}{2mc} \left( \frac{dP}{dr} + \kappa \frac{P}{r} \right) \Rightarrow \quad (3.135)$$

$$\frac{dQ}{dr} = \frac{1}{2mc} \left( P'' + \frac{\kappa}{r} P' - \frac{\kappa}{r^2} P \right) \quad (3.136)$$

Denoting  $E = mc^2 + \varepsilon$ , for bound states  $\varepsilon < 0$ ,

$$\begin{aligned} P'' + \frac{\kappa}{r} P' - \frac{\kappa}{r^2} P - \frac{\kappa}{r} \times \left( \frac{P'}{r} + \kappa \frac{P}{r} \right) \\ + (2mc) \left( -mc + \frac{mc^2 + \varepsilon - V}{c} \right) P = 0. \end{aligned} \quad (3.137)$$

$$\kappa = \begin{cases} -l - 1 \\ l \end{cases} \Rightarrow \kappa(\kappa + 1) = \begin{cases} (-l - 1)(-l) \\ l(l + 1) \end{cases} = l(l + 1) \quad (3.138)$$

$\Rightarrow$

$$P'' - \frac{l(l + 1)}{r^2} P + 2m(\varepsilon - V)P = 0, \quad (3.139)$$

the usual non-relativistic equation.

## 3.6 The Dirac-Coulomb Problem

(Darwin 1928, Gordon 1928). Consider

$$V = -\frac{Z}{r} \quad (3.140)$$

For normalized bound states

$$\int_0^\infty r^2 dr (f^2 + g^2) = \int_0^\infty dr (P^2 + Q^2) = 1 \quad (3.141)$$

(3.134)  $\Rightarrow$

$$\begin{cases} \frac{dP}{dr} + \kappa \frac{P}{r} + \left( -mc - \frac{Z}{c} \frac{1}{r} - \frac{E}{c} \right) Q = 0 \\ \frac{dQ}{dr} - \kappa \frac{Q}{r} + \left( -mc + \frac{Z}{c} \frac{1}{r} + \frac{E}{c} \right) P = 0 \end{cases} \quad (3.142)$$

So far  $\hbar = 1$ . Let now  $m = c = 1$ , as well. Then the unit charge  $e = \alpha = 1/137.036$ . Furthermore denote

$$\lambda = \sqrt{1 - E^2} \quad (3.143)$$

$$x = 2\lambda r \quad (3.144)$$

and introduce the new functions  $\phi_1$  and  $\phi_2$  for which

$$\begin{cases} P = \sqrt{1 + E} e^{-\lambda r} (\phi_1 + \phi_2) \\ Q = \sqrt{1 - E} e^{-\lambda r} (\phi_1 - \phi_2) \end{cases} \quad (3.145)$$

Then

$$\begin{cases} \frac{dP}{dr} = \sqrt{1 + E} e^{-\lambda r} \left[ -\lambda(\phi_1 + \phi_2) + \frac{d\phi_1}{dr} + \frac{d\phi_2}{dr} \right] \\ \frac{dQ}{dr} = \sqrt{1 - E} e^{-\lambda r} \left[ -\lambda(\phi_1 - \phi_2) + \frac{d\phi_1}{dr} - \frac{d\phi_2}{dr} \right] \end{cases} \quad (3.146)$$

Straightforward algebra on Eq. (3.142) gives:

$$\begin{cases} \sqrt{1 + E} e^{-\lambda r} \left[ -\lambda(\phi_1 + \phi_2) + \frac{d\phi_1}{dr} + \frac{d\phi_2}{dr} \right] = \\ -\frac{\kappa}{r} \sqrt{1 + E} e^{-\lambda r} (\phi_1 + \phi_2) + \left[ E + \frac{Z}{r} + 1 \right] \sqrt{1 - E} e^{-\lambda r} (\phi_1 - \phi_2) \end{cases}$$

Dividing the top equation by  $\sqrt{1 + E} e^{-\lambda r}$  and the bottom one by  $\sqrt{1 - E} e^{-\lambda r}$  and noting that  $\frac{\partial}{\partial r} = 2\lambda \frac{\partial}{\partial x}$  we get

$$\begin{cases} -\lambda(\phi_1 + \phi_2) + 2\lambda \left( \frac{d\phi_1}{dx} + \frac{d\phi_2}{dx} \right) = \\ -\frac{\kappa}{r}(\phi_1 + \phi_2) + \left[ E + \frac{2\lambda Z}{x} + 1 \right] \sqrt{\frac{1 - E}{1 + E}} (\phi_1 - \phi_2) \\ -\lambda(\phi_1 - \phi_2) + 2\lambda \left( \frac{d\phi_1}{dx} - \frac{d\phi_2}{dx} \right) = \\ \frac{\kappa}{r}(\phi_1 - \phi_2) - \left[ E + \frac{2\lambda Z}{x} - 1 \right] \sqrt{\frac{1 + E}{1 - E}} (\phi_1 + \phi_2) \end{cases}$$

Dividing now by  $2\lambda$ , gives

$$\left\{ \begin{array}{l} \phi'_1 + \phi'_2 = \frac{1}{2}(\phi_1 + \phi_2) - \frac{\kappa}{x}(\phi_1 + \phi_2) \\ \quad + \left[ E + \frac{2\lambda Z}{x} + 1 \right] \frac{1}{2\sqrt{(1+E)(1-E)}} \sqrt{\frac{1-E}{1+E}} (\phi_1 - \phi_2) \\ \phi'_1 - \phi'_2 = \frac{1}{2}(\phi_1 - \phi_2) + \frac{\kappa}{x}(\phi_1 - \phi_2) \\ \quad - \left[ E + \frac{2\lambda Z}{x} - 1 \right] \frac{1}{2\sqrt{(1+E)(1-E)}} \sqrt{\frac{1+E}{1-E}} (\phi_1 + \phi_2) \end{array} \right.$$

Now, remembering the definition of  $\lambda$ , (3.143), the above can be reorganized to

$$\left\{ \begin{array}{l} \phi'_1 + \phi'_2 = \phi_1 \left[ \frac{1}{2} - \frac{\kappa}{x} + \frac{E + \frac{2\lambda Z}{x} + 1}{2(1+E)} \right] \\ \quad + \phi_2 \left[ \frac{1}{2} - \frac{\kappa}{x} - \frac{E + \frac{2\lambda Z}{x} + 1}{2(1+E)} \right] \\ \phi'_1 - \phi'_2 = \phi_1 \left[ \frac{1}{2} + \frac{\kappa}{x} - \frac{E + \frac{2\lambda Z}{x} - 1}{2(1-E)} \right] \\ \quad + \phi_2 \left[ -\frac{1}{2} - \frac{\kappa}{x} - \frac{E + \frac{2\lambda Z}{x} - 1}{2(1-E)} \right] \end{array} \right.$$

Writing down the sum and difference of the above { (sum at top, difference at bottom):

$$\left\{ \begin{array}{l} 2\phi'_1 = \phi_1 \left[ 1 + \left( E + \frac{2\lambda Z}{x} \right) \frac{1}{2} \left( \frac{1}{1+E} - \frac{1}{1-E} \right) + \frac{1}{2} \left( \frac{1}{1+E} + \frac{1}{1-E} \right) \right] \\ \quad + \phi_2 \left[ -\frac{2\kappa}{x} + \left( E + \frac{2\lambda Z}{x} \right) \frac{-1}{2} \left( \frac{1}{1+E} + \frac{1}{1-E} \right) - \frac{1}{2} \left( \frac{1}{1+E} - \frac{1}{1-E} \right) \right] \\ 2\phi'_2 = \phi_1 \left[ -\frac{2\kappa}{x} + \left( E + \frac{2\lambda Z}{x} \right) \frac{1}{2} \left( \frac{1}{1+E} + \frac{1}{1-E} \right) + \frac{1}{2} \left( \frac{1}{1+E} - \frac{1}{1-E} \right) \right] \\ \quad + \phi_2 \left[ 1 - \left( E + \frac{2\lambda Z}{x} \right) \frac{1}{2} \left( \frac{1}{1+E} - \frac{1}{1-E} \right) - \frac{1}{2} \left( \frac{1}{1+E} + \frac{1}{1-E} \right) \right] \end{array} \right. \quad (3.147)$$

As

$$\begin{aligned} \frac{1}{1+E} - \frac{1}{1-E} &= \frac{-2E}{1-E^2} = \frac{-2E}{\lambda^2} \\ \frac{1}{1+E} + \frac{1}{1-E} &= \frac{2}{1-E^2} = \frac{2}{\lambda^2}, \end{aligned} \quad (3.148)$$

$$\left\{ \begin{array}{l} 2\phi'_1 = \phi_1 \left[ 1 + \left( E + \frac{2\lambda Z}{x} \right) \left( \frac{-E}{\lambda^2} \right) + \frac{1}{\lambda^2} \right] \\ \quad + \phi_2 \left[ -\frac{2\kappa}{x} - \left( E + \frac{2\lambda Z}{x} \right) \frac{1}{\lambda^2} + \frac{E}{\lambda^2} \right] \end{array} \right. \quad (3.149)$$

$$\left\{ \begin{array}{l} 2\phi'_2 = \phi_1 \left[ -\frac{2\kappa}{x} + \left( E + \frac{2\lambda Z}{x} \right) \frac{1}{\lambda^2} - \frac{E}{\lambda^2} \right] \\ \quad + \phi_2 \left[ 1 - \left( E + \frac{2\lambda Z}{x} \right) \left( \frac{-E}{\lambda^2} \right) - \frac{1}{\lambda^2} \right] \end{array} \right. \quad (3.149)$$

$$\left\{ \begin{array}{l} \phi'_1 = \phi_1 \left[ 1 - \frac{ZE}{x\lambda} \right] + \phi_2 \left[ -\frac{\kappa}{x} - \frac{Z}{x\lambda} \right] \\ \phi'_2 = \phi_1 \left[ -\frac{\kappa}{x} + \frac{Z}{x\lambda} \right] + \phi_2 \left[ \frac{ZE}{x\lambda} \right] \end{array} \right. \quad (3.150)$$

Introducing the series

$$\left\{ \begin{array}{l} \phi_1 = x^\gamma \sum_{m=0}^{\infty} \alpha_m x^m \\ \phi_2 = x^\gamma \sum_{m=0}^{\infty} \beta_m x^m \end{array} \right. \quad (3.151)$$

$$\left\{ \begin{array}{l} \phi'_1 = x^\gamma \sum_{m=0}^{\infty} (\gamma + m) \alpha_m x^{m-1} \\ \quad = x^\gamma \sum_{m=0}^{\infty} \left[ \alpha_m x^m \left( 1 - \frac{ZE}{x\lambda} \right) - \beta_m x^m \left( \frac{\kappa}{x} + \frac{Z}{x\lambda} \right) \right] \\ \phi'_2 = x^\gamma \sum_{m=0}^{\infty} (\gamma + m) \beta_m x^{m-1} \\ \quad = x^\gamma \sum_{m=0}^{\infty} \left[ \alpha_m x^m \left( -\frac{\kappa}{x} + \frac{Z}{x\lambda} \right) + \beta_m x^m \frac{ZE}{x\lambda} \right] \end{array} \right. \quad (3.152)$$

The coefficients for every power,  $x^{\gamma+m-1}$ , must vanish for the expansion to be true:

$$\left\{ \begin{array}{l} \alpha_m(\gamma + m) = \alpha_{m-1} - \alpha_m \frac{ZE}{\lambda} - \beta_m \left( \kappa + \frac{Z}{\lambda} \right) \\ \beta_m(\gamma + m) = \alpha_m \left( -\kappa + \frac{Z}{\lambda} \right) + \beta_m \frac{ZE}{\lambda}. \end{array} \right. \quad (3.153)$$

If  $\alpha_{m-1}$  is known, these equations gives  $(\alpha_m, \beta_m)$  For  $m = 0$  ( $\alpha_{-1} = 0$  is assumed),

$$\left\{ \begin{array}{l} \gamma\alpha_0 = \alpha_0 \left( -\frac{ZE}{\lambda} \right) - \beta_0 \left( \kappa + \frac{Z}{\lambda} \right) \\ \gamma\beta_0 = \alpha_0 \left( -\kappa + \frac{Z}{\lambda} \right) + \beta_0 \frac{ZE}{\lambda}. \end{array} \right. \quad (3.154)$$

This linear, homogenous pair has solutions if

$$\begin{vmatrix} \gamma + ZE/\lambda & \kappa + Z/\lambda \\ \kappa - Z/\lambda & \gamma - ZE/\lambda \end{vmatrix} = 0 \quad (3.155)$$

$$\gamma^2 - \left(\frac{ZE}{\lambda}\right)^2 - \kappa^2 + \left(\frac{Z}{\lambda}\right)^2 = 0$$

$$\gamma_2 + \left(\frac{Z}{\lambda}\right)^2(1 - E^2) - \kappa^2 = 0$$

$$\gamma^2 = \kappa^2 - Z^2. \quad (3.156)$$

It turn out that

$$\gamma = +\sqrt{\kappa^2 - Z^2} \quad (3.157)$$

is the acceptable solution and

$$\gamma = -\sqrt{\kappa^2 - Z^2}$$

the irregular one (which can't be normalized). Recall that  $Z$  included the proton charge  $e_p = \alpha = 1/137.036$ . For integer  $Z'$ ,

$$\gamma = +\sqrt{\kappa^2 - (\alpha Z')^2} \quad (3.158)$$

The Eq. (3.153b)  $\Rightarrow$

$$\frac{\beta_m}{\alpha_m} = \frac{-\kappa + Z/\lambda}{m + \gamma - ZE/\lambda} = \frac{\kappa - Z/\lambda}{n' - m}, \quad (3.159)$$

In terms of a new quantity

$$n' = \frac{ZE}{\lambda} - \gamma. \quad (3.160)$$

A substitution to (3.153a) gives

$$\alpha_m \left[ \gamma + m + \frac{ZE}{\lambda} + \left( \kappa + \frac{Z}{\lambda} \right) \frac{\kappa - Z/\lambda}{n' - m} \right] = \alpha_{m-1} \quad (3.161)$$

Here

$$\begin{aligned}
& \left[ \gamma + m + \frac{ZE}{\lambda} + \left( \kappa + \frac{Z}{\lambda} \right) \frac{\kappa - Z/\lambda}{n' - m} \right] \\
&= \gamma + m + \frac{ZE}{\lambda} + \frac{\kappa^2 - (Z/\lambda)^2}{n' - m} \\
&= \frac{1}{n' - m} \left[ \left( \gamma + m + \frac{ZE}{\lambda} \right) \left( -\gamma - m + \frac{ZE}{\lambda} \right) + \kappa^2 - (Z/\lambda)^2 \right] \\
&= \frac{1}{n' - m} \left[ -\left( \gamma^2 + 2\gamma m + m^2 \right) + (ZE/\lambda)^2 + \kappa^2 - (Z/\lambda)^2 \right] \\
&= \frac{1}{n' - m} \left[ -\kappa^2 + Z^2 - 2\gamma m - m^2 + \kappa^2 + Z^2 \underbrace{\frac{E^2 - 1}{\lambda^2}}_{=-1} \right] \\
&= -m \frac{2\gamma + m}{n' - m} \Rightarrow
\end{aligned}$$

$$\alpha_m = -\frac{n' - m}{m(2\gamma + m)} \alpha_{m-1}. \quad (3.162)$$

$$\begin{aligned}
\alpha_m &= (-)^m \frac{(n' - m) \dots (n' - 1)}{m!(2\gamma + m) \dots (2\gamma + 1)} \alpha_0 \\
&= \frac{(1 - n')(2 - n') \dots (m - n')}{m!(2\gamma + 1) \dots (2\gamma + m)} \alpha_0.
\end{aligned} \quad (3.163)$$

(3.159)  $\Rightarrow$

$$\left. \begin{aligned} \frac{\beta_m}{\alpha_m} &= \frac{\kappa - Z/\lambda}{n' - m} \\ \frac{\beta_{m-1}}{\alpha_{m-1}} &= \frac{\kappa - Z/\lambda}{n' - m + 1} \end{aligned} \right\} \Rightarrow$$

$$\begin{aligned}
\frac{\beta_m}{\beta_{m-1}} &= \frac{n' - m + 1}{n' - m} \frac{\alpha_m}{\alpha_{m-1}} \Rightarrow \\
\beta_m &= (-)^m \frac{(n' - m + 1) \dots (n')}{m!(2\gamma + 1) \dots (2\gamma + m)} \beta_0.
\end{aligned} \quad (3.164)$$

(3.154b)  $\Rightarrow$

$$\begin{aligned}
\alpha_0 \left( -\kappa + \frac{Z}{\lambda} \right) &= \beta_0 \left( \gamma - \frac{ZE}{\lambda} \right) \Rightarrow \\
\frac{\alpha_0}{\beta_0} &= \frac{\gamma - ZE/\lambda}{-\kappa + Z/\lambda} = \frac{n'}{\kappa - Z/\lambda}.
\end{aligned} \quad (3.165)$$

Comparing the coefficients (3.163)-(3.164) with those of a confluent hypergeometrical function,

$${}_1F_1(a; c; x) = 1 + \frac{a}{c}x + \frac{a(a+1)}{c(c+1)} \frac{x^2}{2!} + \dots, \quad (3.166)$$

$$\begin{cases} \phi_1 = \alpha_0 x^\gamma {}_1F_1(1 - n'; 2\gamma + 1; x) \\ \phi_2 = \beta_0 x^\gamma {}_1F_1(-n'; 2\gamma + 1; x) \\ \quad = \frac{\kappa - Z/\lambda}{n'} \alpha_0 x^\gamma {}_1F_1(-n'; 2\gamma + 1; x). \end{cases} \quad (3.167)$$

For  $x \rightarrow \infty$ ,  ${}_1F_1(a; c; x) \rightarrow e^x$  because

$$\lim_{m \rightarrow \infty} \frac{\alpha_m}{\alpha_{m-1}} = \lim_{m \rightarrow \infty} \frac{-n' + m}{m(2\gamma + m)} \rightarrow \frac{1}{m}. \quad (3.168)$$

Therefore the series must terminate, That happens for  $\phi_2$  with

$$n' = 0, 1, 2, \dots \quad (3.169)$$

( $n' = 0$  is the ground state,  $n' = 1$  the 1<sup>st</sup> excited state, etc.) Thus  $n'$  is the number of nodes in  $\phi_2$  (or in  $g$ )

For  $n' = 0$ , the coefficients of  $\phi_1$  have

$$\begin{aligned} \alpha_m &= \frac{(1 - n') \dots (m - n')}{m!(2\gamma + 1) \dots (2\gamma + m)} \alpha_0 \\ &= \frac{1}{m!(2\gamma + 1) \dots (2\gamma + m)} \alpha_0, \end{aligned}$$

which converges.

Introduce the principal quantum number

$$n = n' + |\kappa|. \quad (3.170)$$

Then the definition of  $n'$ , (3.160), gives

$$\begin{aligned} \frac{ZE_{n\kappa}}{\lambda} &= n' + \gamma \\ E^2 &= \frac{\lambda^2}{Z^2} (n' + \gamma)^2 = \frac{(1 - E^2)(n' + \gamma)^2}{Z^2} \Rightarrow \\ E^2 \left[ 1 + \frac{(n' + \gamma)^2}{Z^2} \right] &= \frac{(n' + \gamma)^2}{Z^2} \Rightarrow \\ E_{n\kappa} &= \left[ 1 + \frac{Z^2}{(n' + \gamma)^2} \right]^{-1/2} \end{aligned} \quad (3.171)$$

The  $\kappa$  occurs only in  $\gamma = \sqrt{\kappa^2 - Z^2}$ ,  $+|\kappa|$  and  $-|\kappa|$  are degenerate for the same  $n!$  For instance for  $n = 2$ ,

$$E_{2s_{1/2}} = E_{2p_{1/2}} < E_{2p_{3/2}}. \quad (3.172)$$

(Note though that with QED accounted for  $E_{2s_{1/2}} > E_{2p_{1/2}}!$ ) An expansion in powers of  $Z^2$  gives (we still have  $c = 1$ )

$$E_{n\kappa} - 1 = \varepsilon_{n\kappa} = -\frac{1}{2} \frac{Z^2}{n^2} + \frac{Z^4}{n^3} \left[ \frac{3}{8n} - \frac{1}{2|\kappa|} \right] + \mathcal{O}(Z^6) \quad (3.173)$$

#### Qualitative conclusions:

- a. Largest stabilization for  $|\kappa| = 1$ .
- b. States with same  $l$  (and  $n$ ) but different  $j$  are *spin-orbit* split.
- c. For  $|\kappa| = 1$ , both  $f$  and  $g$  diverge at the origin like  $r^{\gamma-1}$ . They remain normalized. The isomer or isotope shifts, proportional to  $\rho(0)$ , grow by a factor of 13 for U.
- d. The radial density,  $P^2 + Q^2$ , has no nodes.
- e. The radial electron density suffers a relativistic contraction.
- f. Normalization is no problem
- g. Continuum, also positron-like can be solved.
- h. Integrals, properties, solvable.
- i. Literature: See Table 2.3 of RTAM I-III (1986, 1993, 2000)

### 3.7 Virial theorems

Literature: See RTAM I-III, Table 2.5.

Fock (1930b), Gupta (1932), Rose & Welton (1952), March (1953), Kim (1967), McKinley (1971), M. Brack (1983).

#### 3.7.1 Non-relativistic case

Let

$$\underline{r} \rightarrow \underline{r}' = \lambda \underline{r} \quad |\underline{r}| = \frac{\underline{r}'}{\lambda} \quad (3.174)$$

$$\begin{aligned} H = T + V &= -\frac{1}{2} \nabla^2 + C r^n \\ &\rightarrow \lambda^2 \left( -\frac{1}{2} \nabla'^2 \right) + C \lambda^{-n} (r')^n \end{aligned} \quad (3.175)$$

$$E(\lambda) = \lambda^2 \langle T \rangle + \lambda^{-n} \langle V \rangle \quad (3.176)$$

$$\frac{\partial E}{\partial \lambda} = \left[ 2\lambda \langle T \rangle - n \lambda^{-n-1} \langle V \rangle \right]_{\lambda=1} = 0 \quad (3.177)$$

$\Rightarrow$

$$2\langle T \rangle = n\langle V \rangle \quad \text{Coulomb: } n = 1 \quad (3.178)$$

Because  $E(\lambda)$  has to be a minimum at  $\lambda = 1$ ,

$$\left(\frac{\partial^2 E}{\partial \lambda^2}\right)_{\lambda=1} = \left[2\langle T \rangle + n(n+1)\lambda^{-n-2}\langle V \rangle\right]_{\lambda=1} > 0 \quad (3.179)$$

$\Rightarrow$

$$\begin{aligned} n\langle V \rangle + n(n+1)\langle V \rangle &> 0, \quad \langle V \rangle < 0 \\ (2+n)n\langle V \rangle &> 0 \end{aligned}$$

$$-2 < n < 0 \quad (3.180)$$

### 3.7.2 Dirac

$$h_D \Phi = E \Phi \quad (3.181)$$

$$h_D = c\underline{\alpha} \cdot \underline{p} 0 \beta mc^2 + V(r), \quad (3.182)$$

$$V(r) = Cr^n \quad (3.183)$$

Bound states considered:

$$\Phi = \begin{pmatrix} \phi_A \\ \phi_B \end{pmatrix}, \quad \langle \phi | \phi \rangle = 1, \quad \langle A | A \rangle + \langle B | B \rangle = 1 \quad (3.184)$$

Again, let  $\underline{r} \rightarrow \underline{r}' = \lambda \underline{r}$ ,  $d\underline{r} \rightarrow \lambda^{-1} d\underline{r}'$ .

$$\Phi(\underline{r}) \rightarrow \lambda^{3/2} \Phi(\underline{r}') \quad (3.185)$$

$$h_D \rightarrow c\lambda \underline{\alpha} \cdot \underline{p} + \beta mc^2 + \lambda^{-n} V(r). \quad (3.186)$$

$$\begin{cases} \langle \Phi' | c\underline{\alpha} \cdot \underline{p} | \Phi' \rangle = \lambda \langle \Phi | c\underline{\alpha} \cdot \underline{p} | \Phi \rangle \\ \langle \Phi' | \beta mc^2 | \Phi' \rangle = mc^2(N_A - N_B) \\ \langle \Phi' | r^{-n} | \Phi' \rangle = \lambda^{-n} \langle \Phi | r^{-n} | \Phi \rangle \end{cases} \quad (3.187)$$

$$E(\lambda) = \lambda \langle c\underline{\alpha} \cdot \underline{p} \rangle + \lambda^{-n} \langle V \rangle + mc^2(N_A - N_B) \quad (3.188)$$

$$\left(\frac{\partial E}{\partial \lambda}\right)_{\lambda=1} = 0 \quad \Rightarrow \quad \boxed{\langle T \rangle = n\langle V \rangle} \quad (3.189)$$

For  $n = -1$ ,

$$\langle T \rangle + \langle V \rangle = c \langle \underline{\alpha} \cdot \underline{p} \rangle + \langle V \rangle = 0 \quad (3.190)$$

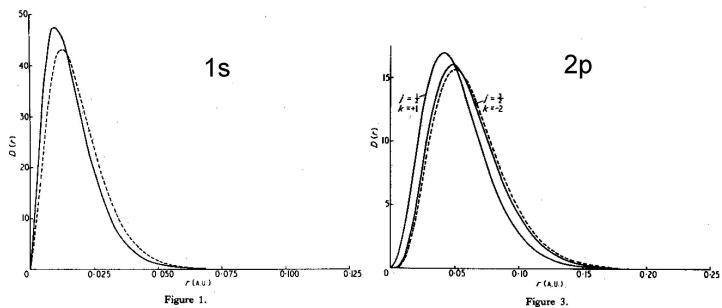
$$\left(\frac{\partial^2 E}{\partial \lambda^2}\right)_{\lambda=1} \Rightarrow [n(n+1)\lambda^{-n-2}\langle V \rangle]_{\lambda=1} > 0 \quad (3.191)$$

$$\langle V \rangle < 0 \Rightarrow n(n+1) < 0 \Rightarrow -1 < n < 0. \quad (3.192)$$

For  $n = -1$ ,

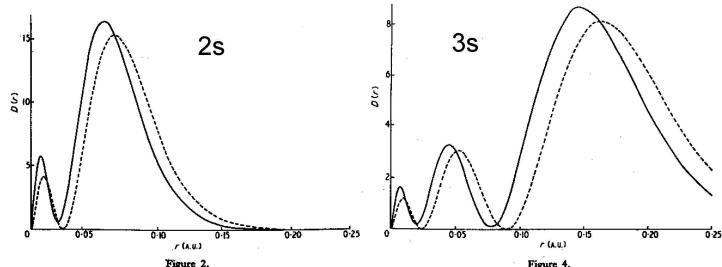
$$\begin{aligned} E &= \langle T \rangle + \langle V \rangle + mc^2(N_A - N_B) \\ E &= mc^2(N_A - N_B). \end{aligned} \quad (3.193)$$

$$E = mc^2\langle \beta \rangle \quad (3.194)$$

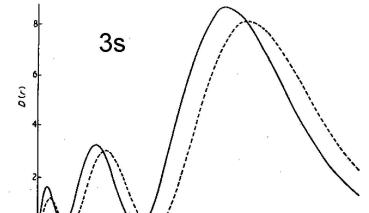


2p

Figure 3.



2s



3s

Figure 3.1: Radial electron densities for the 1s, 2s, 2p and 3s states in a hydrogen-like atom with  $Z = 80$ . The dotted curve denotes the non-relativistic density and the solid curve the relativistic density. Reproduced with permission from V.M. Burke and I.P. Grant, *Proc. Phys. Soc. (London)* **90** (1967) 297-314.

From Figure (3.1) it is seen that the relativistic contraction is of the order for the states 1s, 2s, 2p<sub>1/2</sub> and 3p, whereas the contraction of 2p<sub>3/2</sub> is considerably lesser. The figures 2 and 4 (inside (3.1)) show that 2s and 3s are procentually contracted as much as 1s is. The same conclusion can be drawn for all s-electrons up to the valence shell in a many-electron atom. The p-shells also contract in the same way, but not as much.